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NIOSH HEALTH HAZARD EVALUATION FOR d-LIMONENE

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d-Limonene, a chemical derived from citrus fruits, is a component of solvents often used in the Air Force in place of more hazardous solvents Citrikleen HD and 3M Natural Cleaner were the two d-limonene-containing solver' evaluated by NIOSH in this study. NIOSH developed a sampling method and founc ectable airborne levels of d-limonene during the processes studied. They could not find, however, any clear association between exposure and health hazards in this limited study. Consequently, there was no recommended exposure limit established. Base BEEs should ensure that operations involving the use of d-limonene are evaluated to determine the potential for exposure to workers. If dermal exposure is possible, rubber (butyl or nitrile) gloves, a rubber apron, a face shield, and splash proof goggles should be required as necessary. Workers must also be educated as to the hazards associated with these materials and the reporting requirements should they develop dermatitis.

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SUMMARY

On December 17, 1991, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Brooks Air Force Base Armstrong Laboratory, Occupational Medicine Division, to evaluate occupational exposures and health consequences associated with the use of d-limonene-based cleaning solvents at U.S. air force bases (AFB). d-Limonene is a "natural" hydrocarbon obtained from citrus peels and is a potential replacement for chlorofluorocarbons and other halogenated solvents in a number of industrial and commercial applications. The request was initiated because of the increasing use of d-limonene-based chemicals in AFB operations and the sparsity of occupational health information concerning this chemical. A NIOSH Recommended Exposure Limit (REL) has not been established for d-limonene.

In response to this request, NIOSH investigators conducted an extensive literature search regarding potential health hazards associated with d-limonene and determined an appropriate sampling and analytical method for assessing airborne concentrations of d-limonene. On August 31, 1992, NIOSH investigators conducted an initial site visit at the Robins Air Logistics Center (ALC) in Warner Robins, Georgia. During the site visit, manufacturing processes and chemical-handling practices were reviewed at various shops where a d-limonene-based degreasing solvent (Citrikleen HD) is used in unventilated open surface tanks. An environmental monitoring strategy was developed by identifying specific activities where potential exposures could occur. Material Safety Data Sheets (MSDSs) were obtained for chemicals used in these shops, and industrial hygiene data collected by the ALC Bioenvironmental Engineering office were reviewed.

On October 28-29, 1992, NIOSH industrial hygienists conducted environmental monitoring to assess worker exposure to d-limonene and other components (butyl carbitol, ethanolamine) of Citrikleen HD at ALC Shops 169 (Cable and Tubing, 12 employees) and 76 (Wheel and Tire, 2 employees). Activity specific exposures during the use of a d-limonene-based (70%) aerosol cleaning agent in Shop 169 were also evaluated. Workplace observations regarding the use of personal protective equipment and housekeeping in these shops were made during the site visit.

On December 17-18, 1992, a NIOSH Medical Officer conducted confidential interviews with 14 workers and 1 supervisor from Shops 169 and 76. ALC Base medical records of employees in these shops were reviewed, and the ALC Base Chief Medical Officer was interviewed.

The highest concentration of d-limonene detected was a one-hour time-weighted average (TWA) of 114 parts per million (ppm), obtained from a Shop 76 employee cleaning aircraft wheel hubs. A one-hour TWA exposure of 14 ppm was detected on a

personal sample obtained from a Shop 76 employee drying and polishing the cleaned wheel hubs. The highest concentration of d-limonene detected during personal sampling in Shop 169 was a 35 minute TWA of 5.2 ppm, obtained from an employee using the d-limonene-based aerosol cleaning agent. All other personal sample results from Shop 169 were below 1 ppm. All butyl carbitol sampling results were either below the limit of detection (LOD) or between the LOD and the limit of quantitation. A recommended exposure limit (REL) has not been established for butyl carbitol. Monoethanolamine was detected on only one sample; a six-hour TWA of 0.1 ppm was found on an area sample obtained from behind the Citrikleen HD tank in Shop 169. The NIOSH REL for monoethanolamine is 3 ppm as a 10-hour TWA and 6 ppm as a 15-minute short term exposure limit (STEL). Diethanolamine was not detected on any of the samples collected.

Employee adherance to good personal protective equipment practices (gloves, eye/face protection) when handling the d-limonene-based solvents was sporadic in Shop 169. The Robins AFB Bioenvironmental Engineering Industrial Hygiene department has implemented a system to ensure base facilities are routinely assessed and that all new chemicals are evaluated.

Review of the illness and injury log maintained by the safety department did not uncover any reports related to d-limonene use. Individual employee medical records confirmed the absence of reported d-limonene-related symptomatology. Two of fourteen workers (14%) reported experiencing a disorder suggestive of allergic contact dermatitis (a rash similar to that of poison-ivy) following exposure to Citrikleen HD. Neither of these workers had reported for medical care. Neither worker had a rash at the time of the interview.

Half of the fourteen workers interviewed described an increase in skin dryness since d-limonene-based materials began to be used. None had reported this as a work related symptom, and only a few used skin lotions to alleviate the dryness.

Environmental sampling found detectable airborne levels of d-limonene during various parts cleaning activities. The potential health hazard associated with exposure to the measured concentrations of d-limonene, however, is not clear. The potential exists for dermal exposure to d-limonene at both maintenance shops during metal degreasing activities. Two self-reported cases of possible allergic contact dermatitis associated with the use of d-limonene-containing materials suggest the need for strict adherance to the use of gloves when working with these materials. From a general industry standpoint, additional industrial hygiene and medical data, as well as vigilant surveillance, is necessary as the use of d-limonene-based cleaning agents increases. Specific recommendations are provided in the Recommendation section of this report.

KEYWORDS: SIC 3721 (Aircraft) d-limonene, butyl carbitol, ethanolamine, diethanolamine, degreasing operations, allergic contact dermatitis

INTRODUCTION

NIOSH received a request on December 17, 1991, from the Brooks Air Force Base (AFB) Armstrong Laboratory, Occupational Medicine Division, to evaluate the use of d-limonene-based cleaning solvents. On August 18, 1992, Air Force representatives identified Robins Air Logistics Center (ALC) in Warner Robins, Georgia, as an appropriate site for the NIOSH evaluation.

On August 31, 1992, NIOSH industrial hygienists reviewed activities involving the use of a d-limonene-containing solvent (Citrikleen HD) at Robins ALC. NIOSH investigators conducted a second site visit on October 28-29, 1992, to assess personal exposures to d-limonene and other components of Citrikleen HD and evaluate engineering controls, personal protective equipment, and chemical handling practices. On December 17-18, 1992, NIOSH conducted confidential medical interviews with employees who work with Citrikleen HD and reviewed base medical records.

Interim reports describing preliminary findings, recommendations, and future actions were sent to Brooks AFB and Robins ALC representatives on October 5, 1992, and March 18, 1993.

BACKGROUND

d-Limonene

d-Limonene is a naturally occurring chemical, has a pleasant lemon-like odor, and is found in citrus fruit, spices, and other foods.[1] d-Limonene is one of two chemical forms (stereoisomer) of limonene and is a member of a large class of natural hydrocarbons referred to as terpenes (d-limonene is a monoterpene). The other form of limonene is called l-limonene, and a mixture of the two isomers is known as dipentene. d-Limonene is listed on the Food and Drug Administration's Generally Recognized as Safe (GRAS) list, is widely used as a flavor and fragrance additive in perfumes, soaps, foods, chewing gum and beverages, and is the most widely distributed monoterpene.[2-6] The use of d-limonene, and other terpene-based materials, as industrial degreasing and cleaning agents is increasing as stratospheric ozone-depleting chemicals such as chlorofluorocarbons (CFCs) are phased out and pressure is increased to reduce occupational exposure and environmental releases of chlorinated solvents.[7-8] In 1990-91, Florida produced over 15 million tons of d-limonene.[9] The principle use is not as a solvent, however, as the majority of d-limonene produced is used in the flavor and fragrance industry.[10] The bulk of naturally derived d-limonene is obtained from the high-vacuum fractional distillation and/or extraction of citrus oils (citrus oils are obtained from discarded lemon and orange pulp and peels), and there are an estimated 20-30 manufacturers of d-limonene.[3,8,10-11]

Terpene compounds, including d-limonene, are noncorrosive, low-foaming, relatively nonreactive, and low temperature-effective materials with a high solvency of greases and oils.[8] However, they are not water soluble, and surfactant must be added prior to

addition to water. Although d-limonene is an attractive potential substitute for many degreasing operations, some process changes do require significant capital investments to make the necessary equipment modifications. A major reason for the equipment changes is because terpenes are combustible and have low odor thresholds.[8,12] d-Limonene has a flash point of 118°F and a lower explosive limit of 0.7%.[4]

The odor threshold of d-limonene is reported to be as low as 1 part per billion (ppb).[8] In addition to the fire safety concerns, required compliance with military specifications and the generation of waste water (rinse effluent) may affect widespread acceptance of d-limonene-based products for certain applications (e.g., printed circuit board manufacture).[8]

Citrikleen HD and 3M Natural cleaner

Citrikleen HD is a water soluble citrus-based solvent cleaner and degreaser that contains 20-30% d-limonene, 1-5% monoethanolamine and diethanolamine, and 5-10% butyl carbitol. Citrikleen HD is a clear amber liquid with a citrus odor and has a pH of 11.2. Because of a desire to find alternatives to chlorinated solvents such as trichloroethylene and o,m,p-dichlorobenzene, and the need to phase out chlorofluorocarbon (CFC) solvents, Robins ALC personnel were interested in the use of this material as a cleaning solvent.

3M Natural Cleaner is a citrus-based cleaner that is dispensed from hand held aerosol spray cans. The aerosol, intended for industrial use only as a general purpose cleaner, contains 70-80% d-limonene and uses a propane propellant.

Facility Description

The Robins ALC provides depot-level maintenance support for the F-15, C-141, and C-130 aircraft. The base is middle Georgia's largest employer, with approximately 20,000 civilian and 5,000 military personnel. Civilian employees are represented by the American Federation of Government Employees (AFGE), Local 987. There are 44 employees in the Bioenvironmental Engineering group, which provides occupational health (3 physicians), industrial hygiene, and environmental services. Safety and fire protection are separate functions.

Process Description

<u>Shop 169 (Cable and Tubing)</u>

The Cable and Tubing shop fabricates aluminum, stainless steel, and titanium tube assemblies from 1/8 to 4.5 inches in diameter. The shop is located within a very large warehouse adjacent other maintenance, fabrication, and painting shops. Tubing is cleaned, by soaking only, with Citrikleen HD at ambient temperature both before and after working (bending, cutting, and shaping). Parts are soaked in an open and unvented 100 gallon tank for 10-30 minutes and then rinsed in an adjacent tank of hot

water for each cleaning cycle. Citrikleen HD usage is about one 55 gal. drum per month. A pneumatic pump is used to transfer solvent from the drum to the degreasing tank. Chemical loss is through evaporation, dragout during removal of parts, or residual loss from a rotating skimmer that is mounted on the top of the tank to remove grease and other impurities from the solvent surface. The product, used undiluted, has been used in the shop since December 1991. The tank, located at the back of the shop against a wall, had not been drained or cleaned since being placed into service. The tank was equipped with an air-operated pump, which drains the tank directly to a waste solvent vessel. There was no lid or cover for the tank, and it was open to the shop environment at all times. Twelve employees work in the shop, and the supervisor estimates the tank is used about 5 hours/day, although the majority of this time is unattended soaking of parts. Employees are required to wear personal protective equipment (PPE) consisting of rubber gloves and safety glasses. Neoprene gloves are also occasionally used. Respirators are not required for employees using the Citrikleen HD tank. 3M Natural Cleaner is used approximately 10 minutes per day to clean table tops, equipment, and tubing. Gloves are not typically worn by employees using the aerosol spray cleaner. Citrikleen HD and the 3M Natural Cleaner are the only chemicals used in this shop.

Shop 76 (Wheel and Tire)

The Wheel and Tire shop is in a small (3500 ft^2), single story (sloped roof 12' - 20') building on the Military side of the ALC and is operated by Air Force personnel. Citrikleen HD has been used in the shop to clean aircraft wheel hubs (magnesium/aluminum) since 1988. A 60-gallon unvented tank with a lid is used to contain the cleaning solvent. The wheel hubs are soaked for approximately 5 minutes in a Citrikleen HD/water mixture (1:1) at ambient temperature. Cleaning is very labor intensive and, after soaking, the hubs are vigorously brushed while still in the tank. The hubs are then manually lifted out of the tank where they are further polished and dried. Cleaning wheel hubs requires two workers and is typically conducted as a batch process. That is, cleaning is not conducted until at least 5 or 6 hubs accumulate, and then they are all completed at one time. Wheel and Tire employees estimated that cleaning hubs with Citrikleen HD entails approximately 1-2 hours/week. The tank lid is closed when it is not in use.

The shop is air-conditioned and has a comfort fan for employees to use at their discretion. Workers wear rubber gloves, rubber aprons, and face-shields when the tank is in use. Respirators are not required or used by employees working with Citrikleen HD. The tank is emptied 2-3 times a year by manually pumping the waste solvent into a drum.

The shop was in the process of replacing the tank with a high pressure automated spray washer that uses a non-solvent detergent. The spray washer is currently used successfully at other ALC bases for cleaning wheel hubs and will reduce labor requirements as well as hazardous waste.

EVALUATION PROCEDURES

Environmental

Air Sampling

The processes that were monitored were selected based on an assessment of the chemicals in use, employee work practices, and controls utilized. Activity specific monitoring was conducted to assess the impact of certain tasks on airborne exposures.

On October 28-29, 1992, environmental monitoring was conducted to assess airborne area levels and personal exposures to the various components of Citrikleen HD in Shops 169 and 76. The monitoring was conducted utilizing established analytical protocols (NIOSH analytical methods) where available.[13] Calibrated air sampling pumps were attached to selected workers and connected, via tubing, to sample collection media placed in the employees' breathing zone. Monitoring was conducted throughout the employees' work-shift unless task-specific sampling was conducted. Area samples were collected to identify relative levels at various locations, or when the monitoring method was not conducive to personal sampling (e.g., liquid impinger). After sample collection, the pumps were post-calibrated and the samples submitted to the NIOSH laboratory or contract laboratory (Data Chem, Salt Lake City, UT) for analysis. Field blanks were submitted with the samples. Specific sampling and analytical methods used during this survey were as follows:

A. Bulk Samples (Liquid and Air)

Two bulk liquid samples (spent and unused Citrikleen HD) were obtained from Shop 169 for qualitative analysis by gas chromatography with mass spectrometry detection (GC-MSD). The samples were collected to verify major components, determine if any unexpected compounds were present that may impact the air sampling, and compare the results of the two samples. The samples, collected in glass vials with teflon liners, were shipped separate from the air samples to the NIOSH laboratory for analysis.

Two bulk air samples were collected directly over the Citrikleen HD tanks in Shops 169 and 76 and submitted to the NIOSH laboratory for qualitative analysis of volatile organic compounds (VOCs). The samples were collected using constant-volume SKC model 223 low-flow sampling pumps with standard charcoal tubes as the collection media. The samples were desorbed in 1 milliliter (ml) of carbon disulfide and screened by gas chromatography with a flame-ionization detector (GC-FID). Both samples were further analyzed by GC-MSD to identify contaminants.

The samples collected for d-limonene and butyl carbitol were placed on hold pending the results of the bulk sample analyses. This was done to allow for the possible quantitation of unexpected compounds which may be identified in the bulk samples, as well as allow for necessary analytical adjustments if potentially interfering compounds were detected.

B. d-Limonene

Fifteen integrated air samples for d-limonene were collected using constant-volume SKC model 223 low-flow sampling pumps. Nominal flow rates of 50-200 cubic centimeters per minute (cc/min) were used to collect the samples. Sampling time ranged from 15 minutes to 7 hours. The pumps are equipped with a pump stroke counter and the number of strokes necessary to pull a known volume of air was determined during calibration. This information was used to calculate the air per pump-stroke "K" factor. The pump stroke count was recorded before and after sampling and the difference used to calculate the total volume of air sampled. Standard charcoal tubes (100 milligrams front section/50 milligrams backup) were used to collect the d-limonene. Two field blanks were submitted with the samples. After sample collection, each charcoal tube section was desorbed in 1 (ml) of carbon disulfide for a minimum of 30 minutes. Following desorption, each section was analyzed by GC-FID with a 30-m Stabilwax fused silica capillary column. Using the splitless injection mode, 1 microliter (μl) sample aliquots were analyzed.

The analytical method used for d-limonene sampling and analysis was determined by the NIOSH Measurement Research Support Branch, Measurement Development Section. The method is not specific to the d-limonene isomer but determines total limonene (d and l). Analytical recovery and storage stability studies were conducted to verify the validity of the method. Charcoal tubes were spiked at 3 levels (20 micrograms [μg], 60μg, 100μg), six tubes per level, and desorption efficiency was greater than 92% at each level, with a standard deviation of less than 2%. Tubes were analyzed at 7, 14, and 30 days to assess storage stability. Analysis after 30 days showed a desorption efficiency of 93%, indicating stability at these levels for at least 30 days. Mass spectrometry was used to confirm that none of the terpene analytes decomposed during storage on the charcoal tubes or in carbon disulfide.

C. Butyl Carbitol

Thirteen integrated air samples for butyl carbitol were collected by the same monitoring methodology used for the d-limonene samples. Standard charcoal tubes (100 milligrams front section/50 milligrams backup) were used to collect the butyl carbitol. Two field blanks were submitted with the samples. Although no specific NIOSH analytical method exists for butyl carbitol, this chemical had previously been determined using NIOSH method 1403 (Alcohols IV), and this method was followed to collect the samples.[13] After sample collection, each charcoal tube section was desorbed in 1 ml of 5% methanol in dichloromethane for a minimum of 30 minute and then analyzed by GC-FID. A method validation check was conducted and

desorption efficiency determined at three levels, six samples per level. An average desorption efficiency of 86.3% (range: 84.4% - 87.8%) was obtained and applied to all results. Six spiked tubes were analyzed over 30 days with a desorption efficiency of 88.4%, indicating stability for at least 30 days at this level.

D. Monoethanolamine, Diethanolamine

Five integrated area air samples were collected for monoethanolamine and diethanolamine in Shops 169 and 76 using DuPont P-2500 constant-flow air sampling pumps. Nominal flow rates of 0.7 to 1.0 liter per minute (LPM) were used to collect the samples. Sample times ranged from 1 to 6 hours. Sampling and analysis was conducted according to NIOSH method 3509.[13] Standard impingers containing 15 ml of 2mM hexanesulfonic acid were used as the collection medium. After the samples were collected, deionized water was added to adjust the volume back to 15 ml. The samples were transferred to polyethylene scintillation vials and shipped to the NIOSH contract laboratory for analysis by ion chromatography. Two blanks were submitted with the samples.

Medical

Fourteen employees with direct d-limonene-based solvent exposure were identified through the industrial hygiene investigation. Of these, 12 employees work in Shop 169, and two employees work in Shop 76. Records of work-related injuries and illness are maintained in employee medical charts and are also summarized in a log system similar to the OSHA 200 log: When a civilian or military employee presents to a medical clinic for care of a work related illness or injury the employee completes a form describing the nature of the illness or injury. Information from these forms is abstracted and computerized, allowing chronologic and shop specific review. Additionally, the form prompts follow-up by the Safety and/or Military Medical departments. The computer logs from Shops 169 and 76 for the previous two years were reviewed.

Civilian medical records are located at the occupational health clinic, while military medical records are maintained at the base hospital. A chart review of all 14 employee medical records was conducted to identify work-related dermal symptoms, as well as work-related problems in general.

Confidential health interviews were conducted with all 14 employees. Information concerning the frequency and usage of d-limonene-based materials, and any associated dermal symptoms, was elicited. Additional information regarding work-place injuries was obtained.

EVALUATION CRITERIA

General

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff use established environmental criteria for the assessment of a number of chemical and physical agents. These criteria suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It should be noted, however, that not all workers will be protected from adverse health effects if their exposures are below the applicable limit. A small percentage may experience adverse health effects due to individual susceptibility, pre-existing medical conditions, and/or hypersensitivity (allergy).

Some hazardous substances or physical agents may act in combination with other workplace exposures or the general environment to produce health effects even if the occupational exposures are controlled at the applicable limit. Due to recognition of these factors, and as new information on toxic effects of an agent becomes available, these evaluation criteria may change.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs), and 3) the U.S. Department of Labor Occupational Safety and Health Administration (OSHA) standards.(14-16) Often, NIOSH recommendations and ACGIH TLVs may be different than the corresponding OSHA standard. Both NIOSH recommendations and ACGIH TLVs are usually based on more recent information than OSHA standards due to the lengthy process involved with promulgating federal regulations. OSHA standards also may be required to consider the feasibility of controlling exposures in various industries where the hazardous agents are found; the NIOSH recommended exposure limits (RELs), by contrast, are based primarily on concerns relating to the prevention of occupational disease.

d-Limonene Exposure Estimates

As previously noted, occupational exposure limits have not been established for d-limonene, and there is a lack of occupational exposure monitoring data during both the manufacturing and use of this chemical. Additionally, health effect studies concerning the industrial use of d-limonene are not available. However, studies have been conducted to provide qualitative and engineering estimates of the potential for exposure (dermal and inhalation) to d-limonene in industrial operations. These assessments were conducted as part of an extensive evaluation of terpene-based cleaners as potential replacements of CFCs and other stratospheric ozone depleting chemicals.[7-8] Inhalation exposures were estimated based on monitoring data from similar processes with different chemicals (e.g., chlorinated solvents), and adjusting for

vapor pressure differences. Another technique used a vapor generation rate and box dispersion model to estimate d-limonene concentrations. Dermal exposures were estimated based on the skin surface area exposed and the length of exposure.

These estimates suggest that employees handling parts during cold immersion cleaning (tank at ambient temperature) with a 20% d-limonene-based solvent would experience time-weighted average (TWA) inhalation exposures of 0.07-0.79 ppm.[8] The modeling also showed that workers formulating a 90% d-limonene solution would be exposed to TWA concentrations of 13-144 ppm during dedrumming or sampling. The range is wide because of the assumptions and uncertainty associated with estimating exposures using surrogate chemicals or modeling.

Medical: Health effects and Toxicological Review

d-Limonene

Dermatology

The human health effects most commonly reported in association with d-limonene use are dermal drying and allergic contact sensitization. d-Limonene is an irritant which causes both irritation and drying of the skin.[17] d-Limonene is also a well known sensitizer, causing allergic contact dermatitis among several occupational groups, including food handlers (citrus peel oil), painters (turpentine), and carpenters (lemon wood).[17-21] d-Limonene is a prohapten which undergoes an enzymatic or chemical reaction to become a hapten, which then exhibits contact allergenic properties. The necessity of conversion to a hapten may explain the lack of allergenic cross-reactivity to similarly structured compounds in individual patients.[22]

There is conflicting evidence that d-limonene functions as a sensitizing quencher. Cinnamic aldehyde, a derivative of cinnamon oil, and a compound used extensively by the perfume industry, is a contact sensitizer. Reports that d-limonene inhibits cinnamic aldehyde sensitization have led to the use of "pre-quenched" compounds - cinnamic aldehyde to which d-limonene has been added.[23] The use of these hybrid products was thought to decrease the occurrence of sensitization, possibly through competitive inhibition at the receptor level.[24] d-Limonene was similarly shown to decrease the intensity of citral sensitization in guinea pigs, evidence which favors quenching.[25,26] However, recent studies using both guinea pigs and humans did not provide evidence to support a quenching ability of d-limonene.[23]

Therapeutic applications of d-limonene's ability to breach the dermal barrier is the subject of research activity. d-Limonene increased the percutaneous absorption of indomethacin and ketoprofen in rats.[27,28] Serum concentrations of indomethacin increased proportionally as increasing amounts of ethanol were added to a gel ointment containing d-limonene.[27] d-Limonene was reported to be well absorbed dermally in animals, with maximal blood concentrations reached in 10 minutes.[29,30]

Solvents containing 20-35% d-limonene have been used to remove tar and asphalt from burn injury victims presenting to the emergency room.[31-33] In one case series, involving 21 tar/asphalt burn patients between 1980 and 1983 no adverse reactions were reported. The solvent (De-Solv-it, Orange-Sol, Inc. Chandler, AZ) was used both for dermal and ocular injuries. Copious amounts of the solvent were flushed at the injury site and the tar/asphalt removed.

Carcinogenicity: promotion

Animal studies with male rats raised concerns that d-limonene was carcinogenic. Male F344/N rats which were orally dosed had an increased occurrence of uncommon tubular cell adenomas and adenocarcinomas of the kidney. Similar dosing of female F344/N rats, and $B6C3F_1$ mice of both sexes did not result in an analogous increase in kidney lesions.[3] The male rat-specific urinary protein (α_{2u}-globulin) is not produced in the unique strain of rats known as NCI-Black-Reiter (NBR) rats. In an experiment, male F344 and male NBR rats were orally dosed with d-limonene. The F344 male rats developed an increase in hyaline droplets, as well as renal adenomas. No increase in tumors or preneoplastic lesions were observed in the male NBR rats. It was concluded that the species- and sex-specific protein α_{2u}-globulin was necessary for the development of these cytotoxic and carcinogenic responses.[34]

d-Limonene causes a male rat specific nephrotoxicity which manifests as an increase in protein droplets in the proximal tubule cells. This has been termed hyaline droplet nephropathy and, more specifically, α_{2u}-globulin nephropathy.[3,34,35] The major metabolite of d-limonene is d-limonene-1,2-oxide, which associates reversibly with α_{2u}-globulin in the male rat kidney.[34,35] This results in a chemical complex which is more resistant to degradation than α_{2u}-globulin alone, leading to the accumulation of protein in the proximal tubules of male rats.[34,35]

Given the species- and sex-specificity of α_{2u}-globulin to the male rat kidney, the extrapolation of d-limonene rat toxicity data to humans and other species is not appropriate.[34,36,37]

Orange peel oil has more than 100 different terpene components with limonene accounting for more than 95% of the total terpene fraction. Orange peel oil promotes development of mouse skin papillomas and carcinomas when topically applied to skin after the skin has been exposed to 7,12-dimethylbenz[a]anthracene (DMBA). An experiment using topically applied pure d-limonene demonstrated that d-limonene itself was not a mouse skin tumor promoter. It was surmised that some other component in orange peel oil had promotional activity. Neither orange peel oil nor d-limonene manifested promotional activity when mice were orally dosed.[38]

Carcinogenicity: protection

DMBA and nitrosomethylurea both induce rat mammary tumors. d-Limonene inhibits this development when it is fed to rats during the promotion/progression stage of mammary carcinogenesis.[39-42] A laboratory experiment using M600B-immortalized human mammary epithelial cells demonstrated the inhibition of isoprenylation of a subset of cellular growth control-associated proteins. This is presented as a possible explanation of the chemopreventative and chemotherapeutic activities of limonene.[39]

d-Limonene inhibits the tobacco-specific carcinogen 4-(methylnitrosoamino)-1-(3-pyridyl)-1-butanone (NNK) induced neoplasia of the lungs and forestomach of female A/J mice.[43] d-Limonene also reduces the N-nitrosodiethylamine (NDEA) induced carcinogenesis of forestomach tumors and pulmonary adenomas in female A/J mice.[44]

Gallstone dissolution

d-Limonene infusions through chemically resistant tubing were effective in dissolving gallstones *in vivo* in humans, as reported by H. Igimi and colleagues in Japan.[45-47] The most commonly reported side effect was upper abdominal pain. Rhesus monkey experiments using high d-limonene concentrations with better stone dissolution properties, resulted in severe duct inflammation and even death.[47] *In vitro* experiments have shown limonene to be most effective with cholesterol gallstones.[48]

Animal insecticides

d-Limonene is an active component of cat flea/insecticidal spray and dip, which is applied topically to domestic cats.[49,50] In an experimental situation, cats were thoroughly wetted with an insecticidal dip containing 26.9% d-limonene (15 times the manufacturer's recommended dose level). The cats were then air-dryed. Acute clinical toxicologic signs of hypersalivation, ataxia, muscle tremors, and hypothermia were observed. It was theorized that the d-limonene induced severe generalized dermal vasodilation, causing hypothermia and decreased systemic blood pressure. The hypothermia, in turn, may have triggered subsequent muscle tremors and an exaggerated shivering response. The decreased systemic blood pressure may have caused subsequent ataxia. The trauma of being wetted may have produced hypersalivation. These toxicologic signs resolved within 5 hours. Necropsy revealed no gross treatment-related lesions except for self-induced, traumatic dermal abrasions in the scrotal regions of the male cats.[29]

Miscellaneous

Japanese patents for various d-limonene-containing products have been issued. These products include a hair growth stimulant, a deodorant air treatment, a decontaminating agent for radioactive materials, and a skin cleanser (2-40% d-limonene by weight).[51-53] Further information regarding these uses was not available.

Butyl Carbitol

Diethylene glycol monobutyl ether, or butyl carbitol, is one of a class of compounds known as glycol ethers. Because of their unique solvent properties, these compounds have widespread applications that includes surface coatings, dye solvents, ingredients in brake fluids, household cleaners, and solvents for enamels.[4,54] Occupational exposure standards or recommendations for butyl carbitol have not been established. Because of the low vapor pressure of butyl carbitol (0.02 mm Hg), the inhalation hazard is considered to be low unless the material is heated or agitated. Data on the adverse affects on humans as a result of inhalation are not available; repeated-dose (oral) studies, however, suggest that the material may be rather toxic if inhaled or absorbed through the skin in repeated small doses.[11,55] Observations in animals indicate the remote possibility of pulmonary edema, intravascular hemolysis and bone marrow depression with some ether derivatives of diethylene glycols.[11] Butyl carbitol is considered slightly irritating to the skin and is not expected to cause sensitization.[4] Butyl carbitol is absorbed through the skin, but the acute toxicity of exposure by this route is considered to be slight, and exposure must be severe before health effects are expected.[4,11,55]

Ethanolamine, Diethanolamine

Ethanolamine, or monoethanolamine, is a colorless, viscous liquid with an unpleasant, fishy, ammoniacal odor that can be detected at about 2-3 parts per million (ppm).[11] Ethanolamine is a pulmonary irritant in animals, and it is expected that severe exposure will cause the same effect in humans.[56] The liquid applied to human skin for 1.5 hours caused marked erythema.[56] The NIOSH REL for ethanolamine is 3 ppm as a 10-hour time-weighted average (TWA) and 6 ppm as a 15-minute short-term exposure limit (STEL).[14] These recommended exposure levels are based on skin, eye, and respiratory irritation, and central nervous system effects.[14]

Diethanolamine exists either as colorless crystals or as a colorless liquid at ambient temperatures (the melting point is 28°C) and has an ammoniacal odor.[56,57] Diethanolamine is an eye irritant and has caused liver and kidney damage in animals.[56] The NIOSH REL, and OSHA PEL, for diethanolamine is 3 ppm as a 10-hour TWA.[14,16]

RESULTS AND DISCUSSION

Environmental

A. Bulk Samples

Two bulk liquid samples obtained from Shop 169 and two charcoal tube air samples from Shops 169 and 76 were qualitatively analyzed for VOCs. Charcoal tubes obtained during sampling for the d-limonene and butyl-carbitol were placed on hold pending the results of the bulk sample analysis.

The two liquid solvent samples (spent and unused Citrikleen HD) contained similar components and were consistent with the manufacturer's MSDS. The major constituents were limonene, butyl carbitol, and ethanolamine. Other compounds detected in the samples included dipropylene glycol, other terpene compounds, diethanolamine, and a fatty acid ester. This analysis confirmed the compounds suspected to be present and ensured that there were no unforeseen contaminants present in the degreasing solvent.

Bulk air sample LB-A5, obtained directly over the degreasing tank in Shop 169 showed that limonene, and an unexpected compound, methyl ethyl ketone (MEK) were the major constituents. Other terpenes, butyl carbitol, toluene, and hexane were also detected on the sample. As MEK was an unexpected contaminant, the samples collected for limonene quantitation were also analyzed for MEK. Because charcoal tubes are not the media of choice for MEK, and MEK will sometimes react on charcoal to produce a hydrolysis product, the MEK results should be considered minimum concentrations. The source of the MEK was thought to be from solvent use in an adjacent shop where maintenance is conducted on airplane bay doors.

Bulk air sample LB-A6 was obtained directly over the degreasing tank in Shop 76. This sample showed that limonene was the major constituent detected. Additionally, other terpenes, terpene derivatives, and alkyl benzenes were detected. No MEK was found on this sample.

B. d-Limonene, MEK, Total VOCs

The results of the air samples collected for d-limonene are shown in Table 1. As noted above, these samples were also analyzed for MEK. Because minor amounts of other VOCs were detected on all samples except one (sample # L-ST1), total VOCs were also quantitated using limonene as the standard. None of the compounds of interest were detected on the field blanks. All personnel sampled stated that their activities during the sampling period were consistent with those of a normal work day.

In Shop 169, the highest concentration of limonene detected was 5.82 ppm (#L-A2A), in an afternoon sample collected from behind the hot-water rinse tank adjacent the Citrikleen HD tank. The highest concentration detected on a personal sample was 5.20 ppm (#L-P5) from a 35-minute sample obtained during the use of the d-limonene containing aerosol cleaner. A 23-minute personal sample obtained during the transfer of Citrikleen HD from a drum to the tank, using an automatic pump with a hand-held hose, showed a concentration of 0.63 ppm (#L-ST1).

The highest MEK concentration detected in Shop 169 was 2.15 ppm (#L-A1A), in a morning sample collected from behind the hot water rinse tank. The range of MEK concentrations detected (both personal and area) was 0.72 - 2.15. Although MEK can be readily detected by the sense of smell at low concentrations, and workers in

Shop 169 were familiar with the odor of MEK from the adjacent shop, no MEK odors were detected during the sampling period. It is likely that the characteristic citrus odor of the limonene masked the MEK.

At two of the locations sampled in Shop 169, the charcoal tubes were changed during the lunch break to assess relative differences between morning and afternoon samples. The results suggest that MEK concentrations were relatively higher in the morning than the afternoon, and that the converse was true for the limonene samples. One possible explanation is that MEK may have only been used in the adjacent shop in the morning, and that the limonene levels increased in the afternoon as parts soaked with the Citrikleen HD were placed in the hot water rinse tank, thus enhancing volatilization of the limonene.

In Shop 76, a limonene concentration of 114.30 ppm was measured on a one-hour personal sample obtained from an employee cleaning aircraft hubs in the Citrikleen HD tank. As noted in the process description, this activity entails vigorous scrubbing of the wheel hubs while they are submerged in the degreasing solvent. The worker must lean over the tank to conduct this task, often within the envelope of the tank freeboard space. This close contact, continuous use, agitation of the solution, and lack of ventilation contributed to the higher concentration of limonene, relative to Shop 169. A one-hour sample obtained from the worker assisting the employee cleaning the aircraft hubs showed a limonene concentration of 14.63 ppm. This worker would assist with the removal of wheel hubs from the degreasing tank, and then use cloth rags to dry and polish the hubs. The worker conducted this task at a station approximately six feet away from the degreasing tank. The cloth rags were frequently changed and were disposed of in a 55-gallon drum that had been converted into a waste container.

No MEK was detected in the samples collected in Shop 76. Other VOCs were detected on both samples, but were well below the concentration of limonene (e.g., 637.5 milligram per cubic meter [mg/m^3] limonene, 37.56 mg/m^3 other VOCs).

C. Butyl Carbitol

The results of the butyl carbitol sampling are shown in Table 2. None of the samples detected butyl carbitol at a quantifiable level. On six of the thirteen samples, the concentration of butyl carbitol was between the analytical limit of detection and the limit of quantification. This was not an unexpected result, as butyl carbitol comprises only 5-10% of the Citrikleen HD solvent, and, due to the low vapor pressure, is not considered volatile and will not readily evaporate into the air.

D. Ethanolamine, Diethanolamine

Ethanolamine was only detected in one of the five area samples collected. A concentration of 0.10 ppm was found in the sample obtained from behind the Citrikleen HD tank in Shop 169. This correlates with the concentrations found by Robins AFB industrial hygienists during a February 13, 1992, survey. During this survey, ethanolamine concentrations of 0.11 and 0.12 ppm were detected in area samples adjacent the Citrikleen HD tank. No personal samples were collected. The levels detected are well below the 3 ppm NIOSH REL. No diethanolamine was detected in any of the samples collected.

Personal Protective Equipment/Workplace Observations

<u>Shop 169</u>

Safety glasses are required to be worn at all times in Shop 169, and some employees working at the Citrikleen HD tank were observed to wear natural rubber gloves. The use of gloves, however, was sporadic. Face shields and aprons were not worn by employees when working at the Citrikleen HD tank. Housekeeping was in good order throughout the shop. The Citrikleen Tank, however, was not labeled with the name of the contents and appropriate hazard warnings. Visible discoloration of the wall behind the Citrikleen HD tank was observed; as mentioned, the tank is not covered when it is not being used, and there is no local exhaust ventilation. During the transfer of new Citrikleen HD from a drum to the degreasing tank, the operator wore eye protection and rubber gloves. There are no provisions for rinsing and decontaminating gloves in the shop. Quick drenching facilities (emergency eye wash) are located in the center of the shop. Comfort fans were operational during the site visit. Smoking is not allowed in Shop 169. Most employees bring their lunch and consume food and beverages at their work stations.

<u>Shop 76</u>

Air Force Technical Orders regarding the use of the Citrikleen HD tank for cleaning aircraft wheel hubs, including personal protective equipment (PPE) requirements, were being followed at Shop 76. The employee cleaning the wheel hubs at the degreasing tank wore heavy duty rubber gloves, rubber apron, and face shield. Eye protection was not worn. Note that a face shield will not provide unlimited protection from chemicals. Proper goggles should be worn in combination with face shields where chemical splash hazards exist. The employee wiping down the cleaned wheel hubs wore rubber gloves and eye protection.

The shop has comfort fans and an air-conditioner. As noted, the Citrikleen HD tank is only used 1-2 hours per week, and is covered when not in use. Smoking is not allowed in the shop, and an emergency eye wash station has been installed.

During the October 28-29, 1992, survey, shop personnel indicated that the Citrikleen HD station would soon be replaced with an automated spray wash system. During the medical evaluation phase of the project (December 17-18, 1992), the new cleaning system was being installed. This system provides fully enclosed, hot water, high pressure cleaning of aircraft wheel hubs. A powdered detergent is used, which does contain some d-limonene. The detergent is added to a reservoir where it is mixed with water.

Base Industrial Hygiene Programs

Industrial hygiene services are provided out of the Bioenvironmental Engineering Office. Safety and fire protection are operated out of different departments; however, communication between these functions is good, and information such as accident reports, chemical inventories, etc., is shared. Annual inspections of the 711 identified workplaces are conducted by ALC Base industrial hygienists. These workplaces are categorized as either critical, potential, or non-hazardous. Files are maintained of each workplace, including chemical inventories, reports from investigations, and environmental evaluation data. All new chemicals are reviewed and approved by industrial hygiene prior to use. However, some approved materials (e.g. 3M Natural Cleaner, and other common stock items) may eventually be used in other areas. This use may not be noted by ALC Base Industrial Hygiene until the annual inspection is conducted. A surveillance system, based on supervisor injury reports, medical evaluations, and communication forums (Safety, other offices), is in place to assist in the early detection of potential problems.

Medical

Record Review

Review of the illness and injury log maintained by the Safety Department did not uncover any reports related to the use of d-limonene-containing material. Review of individual employee medical records confirmed the absence of reported symptomatology during or subsequent to the use of d-limonene-based material.

During the medical chart review, diverse finger injuries among workers in the tubing and cable shop were noted. Injuries included a fracture, a partial amputation, and a crush injury.

Employee Interviews

A. Limonene Usage

All 14 employees confirmed that they currently or recently used the Citrikleen HD dip tanks in their respective shops. Shop 76 workers reported 1-2 hours of direct exposure per week. In Shop 169 there was a maximal direct weekly exposure of 2 hours, with reported use of the dip tank varying from "rarely" to "daily." Indirect exposure due to

time spent in the vicinity of the dip tanks was not quantified. In both shops a pair of communal gloves was available for use with the dip tanks; all employees reported using them. Additionally, a face shield and splash apron were used in the wheel and tire shop.

Eleven employees in Shop 169 used a d-limonene-based spray-can cleanser to clean stationary equipment. Frequency of use ranged from once per month to three times per week. Gloves for this task were not specifically available and were never used.

B. d-Limonene Associated Symptomatology

Two of fourteen workers (14%) reported experiencing a disorder suggestive of allergic contact dermatitis (a rash similar to that of poison-ivy) following exposure to Citrikleen HD. Some substances can cause both allergic contact and irritant dermatitis, and the two responses may be indistinguishable. [20] The caustic nature (pH = 11) of Citrikleen HD could be one potential explanation for the symptoms reported. One worker had used the dip tank without gloves when the tank was newly installed and subsequently developed dermatitis. Since that time he used the dip tank infrequently, always with gloves, and has not had a recurrence. The other worker experienced repeated episodes of dermatitis until his job rotation removed him from Citrikleen HD exposure. Neither of these workers had reported for medical care.

Half of the fourteen workers described an increase in skin dryness since d-limonene-based materials began to be used. None had reported this as a work-related symptom, and only a few used skin lotions to alleviate the dryness.

One individual in Shop 76 reported superficial skin sloughing on one hand after an hour of exposure to Citrikleen HD resulting from a hole in his glove. He denied local itching or redness, or other skin or systemic symptoms.

In Shop 169, where the Citrikleen HD tank is not covered, four of twelve workers (33%) reported an increase in nasal or throat irritation since tank installation. Several noted an increase in symptoms when in the vicinity of the tank.

C. Finger Injuries

Five of the twelve Shop 169 employees reported finger injuries requiring medical attention. The Clark & Lewis tube bender was involved in two injuries. One worker sustained local nerve damage after his finger was caught between the machine jaws and an aluminum tube (the aluminum tube flattened, averting more severe damage). Another worker had a soft tissue injury from the mandrel kick-back. The large cable swager was responsible for a soft tissue ("callus") amputation of a finger-tip, and the small cable swager caused a finger-tip fracture due to cable kick-back. The most severe injury occurred when a valve failed on the pre-set machine, causing a severe crush injury with small finger amputation at the proximal phalange.

CONCLUSIONS

A limited industrial hygiene and medical evaluation was conducted to assess the industrial use of a d-limonene-based cleaning solvent at the Robins ALC AFB. The environmental sampling results indicate relatively higher d-limonene concentrations than those predicted by previous modeling studies of cold-cleaning of parts.[8] However, neither tank was provided with local exhaust ventilation, and there is no cover on the Citrikleen HD tank in Shop 169. The potential health hazard associated with exposure to these levels of d-limonene, however, is not clear. From a general industry standpoint, additional industrial hygiene and medical data, as well as vigilant surveillance, is necessary as the use of d-limonene-based cleaning agents increases.

Personal exposures to d-limonene in Shop 76 were considerably greater than those found in Shop 169. This is an understandable finding, as the work tasks are very different at the two shops. Again, the health implications of these exposure levels is not known. The planned process change to an automated parts cleaner will eliminate the use of Citrikleen HD, and a degreasing tank, in this shop.

Airborne concentrations of butyl carbitol, ethanolamine, and diethanolamine, were very low and often below the analytical level of detection. As both the vapor pressures and relative percentages of these materials in the Citrikleen HD solvent are low, this was not an unexpected result. Additionally, according to Citrikleen HD manufacturing representatives, most of the ethanolamine and diethanolamine are neutralized in solution by fatty acids present in the solvent.[58]

The potential exists for dermal exposure to d-limonene at both maintenance shops during the use of the Citrikleen HD tank. The activities entailed close contact with the Citrikleen HD, particularly at Shop 76, and employee adherance to the proper use of PPE was sporadic. This is of particular concern as d-limonene is a skin irritant and sensitizer.[3]

The ALC Base Bioenvironmental Engineering office has developed a good industrial hygiene and medical surveillance program for employees at Robins ALC AFB. This surveillance program may not, however, identify issues such as d-limonene-related allergic contact dermatitis. This is because these problems may not be reported to supervisors for subsequent investigation, or workers may not associate these problems with the d-limonene-based materials. The potential for increasing use of both the Citrikleen HD and the d-limonene-based aerosol cleaner warrant the need to target surveillance at early identification of problems relating to these materials.

RECOMMENDATIONS

As the Citrikleen HD degreasing process in Shop 76 was being replaced during the NIOSH site visit with a different aircraft wheel hub cleaning system, no recommendations regarding this specific activity are made. However, recommendations regarding findings and observations made at this shop which are applicable to other areas are provided.

1. Install a tank cover on the Citrikleen HD tank in Shop 169. This will serve to prevent solvent loss and reduce ambient concentrations due to volatilization when the tank is not in use.

2. Ensure the Citrikleen HD tank is properly labeled with the name of the contents and appropriate hazard warnings.

3. Establish and enforce good personal protective equipment (PPE) practices when using the Citrikleen HD tank. Employees dispensing or transferring solvent at this tank should use rubber (butyl or nitrile) gloves, a rubber apron, face shield, and goggles. Gloves, splash proof goggles, and a face shield should be worn when loading parts at this station. Butyl and nitrile rubber are two types of material identified in the American Conference of Governmental Industrial Hygienists (ACGIH) Guide for Chemical Protective Clothing as having good resistance properties against d-limonene.[59] Personal gloves should be issued to all employees working with limonene since the inside of communally shared gloves are likely to become contaminated during use. The contamination inside the glove may not be enough to induce skin drying, but may be enough to provoke an allergic response. Allergic contact dermatitis may occur after only one exposure, but usually repeated exposure is required. Once this has occurred, the dermatitis will occur on any subsequent exposure. Personal gloves will both help prevent recurrent allergic contact dermatitis among sensitized employees, and will also decrease the likelihood that other employees will become sensitized.

4. Install a glove-washing station in Shop 169 adjacent the Citrikleen HD tank. The temperature in the hot-water rinse tank makes this tank unacceptable for this purpose. Employees should be instructed to rinse and inspect their gloves after each use.

5. Establish a surveillance system to identify any cases of dermatitis resulting from the use of d-limonene-based products. Supervisor and employee awareness of the need to report potential cases will be necessary. A mechanism to identify and track where common stock d-limonene products are used (e.g., 3M Natural Cleaner) will be necessary.

6. Employees working with d-limonene-based solvents should be instructed that d-limonene will cause skin drying upon contact and may, among some individuals, provoke an allergic contact dermatitis. A simple explanation of allergic contact dermatitis may be made by referring to poison ivy: Poison ivy contains an allergen to which 80% of the population is sensitized; the other 20% are not sensitized and do not get the characteristic rash upon exposure. While d-limonene will cause an allergic contact dermatitis among some workers, the percentage of individuals who would be affected is uncertain. In this small study, two of fourteen (14%) workers had a history suggestive of allergic contact dermatitis resulting from exposure to a d-limonene-based degreasing agent. Irritant dermatitis or caustic effects could also potentially explain the symptoms. Further studies are needed to determine how many individuals, on a population basis, may be expected to develop dermatitis.

7. The machinery in the tubing and cable shop should be evaluated for further guarding, and controls implemented to prevent finger injuries.

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For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table 1
Air Sampling Results: Limonene, MEK, Other VOCs
Robins Air Force Base
October 29, 1992
HETA 92-101

Task Monitored and Location	Sample #	Sample Time (min)	Contaminants Sampled	Concentration	
				ppm	mg/m³
Area Sample Adjacent Citrikleen Tank Shop 169	L-A1	07:43 - 11:34 (231)	Limonene MEK Other VOCs	0.45 2.15	2.51 6.33 0.48
	L-A1A	11:37 - 15:15 (218)	Limonene MEK Other VOCs	3.56 0.91	19.79 2.69 0.27
Area Sample Behind Citrikleen Hot Water Rinse Tank Shop 169	L-A2	07:48 - 11:43 (235)	Limonene MEK Other VOCs	2.85 1.58	15.85 4.66 0.93
	L-A2A	11:45 - 15:16 (211)	Limonene MEK Other VOCs	5.82 0.72	32.35 2.11 1.05
Area Sample, Center of Shop 169, 25 ft. from Citrikleen Tank	L-A3	07:53 - 15:15 (442)	Limonene MEK Other VOCs	0.14 0.98	0.77 2.89 0.33
Area Sample, Left side of Shop 169, 25 ft. from Citrikleen Tank	L-A4	07:54 - 15:15 (441)	Limonene MEK Other VOCs	0.10 0.93	0.53 2.73 0.27
Personal Sample, Metal Tube Maker, B-Team, Shop 169	L-P1	08:09 - 15:24 (435)	Limonene MEK Other VOCs	0.26 0.77	1.43 2.28 0.18
Personal Sample, Metal Tube Maker, C-Team, Shop 169	L-P2	08:47 - 11:30 11:48 - 15:24 (379)	Limonene MEK Other VOCs	0.14 0.82	0.78 2.43 0.49
Personal Sample, Metal Tube Maker, C-Team, Shop 169	L-P3	08:53 - 15:24 (391)	Limonene MEK Other VOCs	0.15 0.76	0.85 2.25 0.45
Personal Sample Sheet Metal Mechanic A-Team, Shop 169	L-P4	08:39 - 11:29 12:11 - 15:24 (363)	Limonene MEK Other VOCs	0.77 0.85	4.28 2.50 0.50
Personal Sample Cleaning with Limonene Based Aerosol, Shop 169	L-P5	08:32 - 09:07 (35)	Limonene MEK Other VOCs	5.20 1.47	29.00 4.33 0.58
Personal Sample, Transfer of Citrikleen from Drum to Tank, Shop 169	L-ST1	13:09 - 13:32 (23)	Limonene MEK Other VOCs	0.63 0.77	3.52 2.26 ND
Area Sample, Adjacent Citrikleen Tank, Shop 76	L-A5	09:54 - 11:05 (70)	Limonene MEK Other VOCs	11.58 ND	64.4 ND 4.43
Personal Sample, Cleaning Wheel Hubs (4 total) in Citrikleen Tank, Shop 76	L-P6	09:57 - 10:56 (59)	Limonene MEK Other VOCs	114.30 ND	635.70 ND 37.56
Personal Sample, Final Polish and Dry of Wheel Hubs, Shop 76	L-P7	09:59 - 10:59 (60)	Limonene MEK Other VOCs	14.63 ND	81.39 ND 4.35

NOTES:

1. ppm = parts of gas or vapor per million parts of air
2. mg/m³ = milligrams of contaminant per cubic meter of air
3. ND = none detected (level of detection = 0.5 microgram (µg) per sample for VOCs, 1 µg for MEK, and 0.5 µg for Limonene)
4. Reported results for MEK should be considered estimated minimum concentrations

Table 2
Air Sampling Results: Butyl Carbitol
Robins Air Force Base
October 29, 1992
HETA 92-101

Task Monitored and Location	Sample #	Sample Time (min)	Concentration	
			ppm	mg/m³
Area Sample Adjacent Citrikleen Tank Shop 169	BC-A1	07:43 - 11:34 (231)	(0.06)	(0.43)
	BC-A1A	11:37 - 15:15 (218)	(0.04)	(0.23)
Area Sample Behind Citrikleen Hot Water Rinse Tank Shop 169	BC-A2	07:48 - 11:43 (235)	<0.06	<0.41
	BC-A2A	11:45 - 15:16 (211)	(0.14)	(0.92)
Area Sample, Center of Shop 169, 25 ft. from Citrikleen Tank	BC-A3	07:53 - 15:15 (442)	<0.02	<0.11
Area Sample, Left side of Shop 169, 25 ft. from Citrikleen Tank	BC-A4	07:54 - 15:15 (441)	<0.03	<0.22
Personal Sample, Metal Tube Maker, B-Team, Shop 169	BC-P1	08:09 - 15:24 (435)	(0.07)	(0.47)
Personal Sample, Metal Tube Maker, C-Team, Shop 169	BC-P2	08:47 - 11:30 11:48 - 15:24 (379)	<0.02	<0.12
Personal Sample, Metal Tube Maker, C-Team, Shop 169	BC-P3	08:53 - 15:24 (391)	<0.02	<0.15
Personal Sample Sheet Metal Mechanic A-Team, Shop 169	BC-P4	08:39 - 11:29 12:11 - 15:24 (363)	<0.01	<0.07
Area Sample, Adjacent Citrikleen Tank, Shop 76	BC-A5	09:54 - 11:05 (70)	<0.14	<0.90
Personal Sample, Cleaning Wheel Hubs (4 total) in Citrikleen Tank, Shop 76	BC-P6	09:57 - 10:56 (59)	(0.27)	(1.76)
Personal Sample, Final Polish and Dry of Wheel Hubs, Shop 76	BC-P7	09:59 - 10:59 (60)	(0.12)	(0.79)

NOTES:

1. ppm = parts of gas or vapor per million parts of air
2. mg/m³ = milligrams of contaminant per cubic meter of air
3. () = concentration detected was between the analytical level of detection and the level of quantification
4. < = less than (no contaminant detected), the concentration listed is the analytical level of detection. The analytical level of detection for butyl carbitol was 5 micrograms (µg) per sample and the level of quantification was 20 µg per sample.